

First-principles investigation of hydrogen adatoms on uniaxially strained graphene

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We have performed first-principles studies on adsorption patterns of hydrogen adatoms on uniaxially strained graphene. Our simulation reveals that the adsorption energy of adatoms are sensitive to the strain. Hydrogen adatoms on zigzag strained graphene tend to form a chain-like adsorption patterns perpendicular to the strain direction, but those under armchair strain cannot form any long-range chain pattern. We explain our results in terms of a tight-binding model and the electronic structure of strained graphene. These anisotropic adsorption behaviors under uniaxial strain suggest methods for obtaining regular adsorption patterns and tailoring the electronic structure of graphene.

Graphene, a single layer of graphite, has ignited tremendous research interest because of its unique electronic structure and associated exciting electrical, thermal, and optical properties [1–4]. However, to realize devices based on graphene we have to develop methods of tailoring its electronic structure. One promising approach is to adsorb chemical groups and adatoms onto graphene to modulate its electronic and optical properties [5–10], giving rise to the large-scale production of functionalized graphene [11–13]. For example, a finite and tunable band gap can be obtained by the adsorption of various chemical groups, making it possible to use graphene for bipolar devices [6, 14, 15]. However, a known drawback of this approach is that these adsorption patterns are usually irregular, resulting in unwanted scattering, severely decreasing the mobility of free carriers. Therefore, understanding the mechanism behind these adsorption patterns and how to control them are crucial for developing broader applications of graphene.

On the other hand, graphene exhibits excellent mechanical properties; recent experiments have shown that well-prepared graphene can sustain uniaxial strain up to 15%, making graphene one of the most stretchable crystalline structures known [16, 17]. We can capitalize on the impressive mechanical characteristics of graphene to develop ways of modulating the electronic structure, motivating us to study the adsorption of chemical groups or adatoms on stretched graphene. Because of the broken symmetry, we expect that the adsorption preference of adatoms on stretched graphene will be significantly modified, *i.e.*, the formation energy of adsorption patterns may be strongly anisotropic. This would give hope of controlling the adsorption process to form regular patterns.

In this Letter, we focus on the strain effects on hydrogen adatoms because recent experiments have shown that hydrogen atoms can be efficiently and precisely adsorbed onto graphene [5, 18]. First-principles simulations are carried out to study the adsorption energy of hydrogen adatoms on graphene with +5% stretch. We examine two basic uniaxial strain directions, armchair and zigzag. The energetically favored adsorption patterns of hydrogen adatoms under zigzag strain tend to form a chain-like configuration that is always perpendicular to the strain

direction, but those under armchair strain cannot hold the regular chain-like pattern for adatoms more than five. The regular chain-like pattern obtained by zigzag strain can be well explained by the tight-binding model and the randomness of the adsorption pattern under armchair strain is attributed to the resonance between the atomistic modulation and electrons around the Dirac cone.

We perform our simulations by employing density functional theory (DFT) within the local density approximation (LDA) through the Quantum Espresso simulation package [19] with norm-conserving pseudopotentials [20, 21]. To avoid artificial interactions between neighboring graphene layers, we set the inter-layer distance to be 1.2 nm. The force and stress are fully relaxed according to DFT/LDA. In order to mimic isolated patterns of adsorbed hydrogen atoms, we choose supercells of sufficient size. Here we use rectangular supercells composed of 96 carbon atoms, but the geometry of the supercell is different for each strain condition. As shown in Fig. 1 (a), the supercell for armchair strain has 24 carbon atoms along its zigzag axis and 4 carbon atoms along its armchair axis. The supercell for zigzag strain shown in Fig. 1 (b) has 12 carbon atoms along its zigzag axis and 8 carbon atoms along its armchair direction. These choices of supercells are based on our later simulation which reveals that adsorption patterns usually prefer to be perpendicular to the strain direction. As a result, the above supercell choices can maximize the distance between adsorption patterns and minimize the interaction between neighboring ones. A plain-wave basis is used with an energy cutoff of 816 eV. A 2x2x1 k-point sampling grid is employed for the energy convergence.

Our simulation procedure to find the energetically preferred adsorption pattern is as follows: We affix the first hydrogen atom above a host carbon on a graphene sheet and fully relax the structure. Then we determine the adsorption energy of a second adatom at each of the nearest and second nearest neighbor positions by comparing the total energy obtained from DFT/LDA. Actually only the nearest neighboring positions need to be considered because our simulations and previous results [18] show that these nearest neighbor positions are always more energetically preferred. Moreover, the nearest neighbor adatoms prefer to alternate above and below the graphene layer

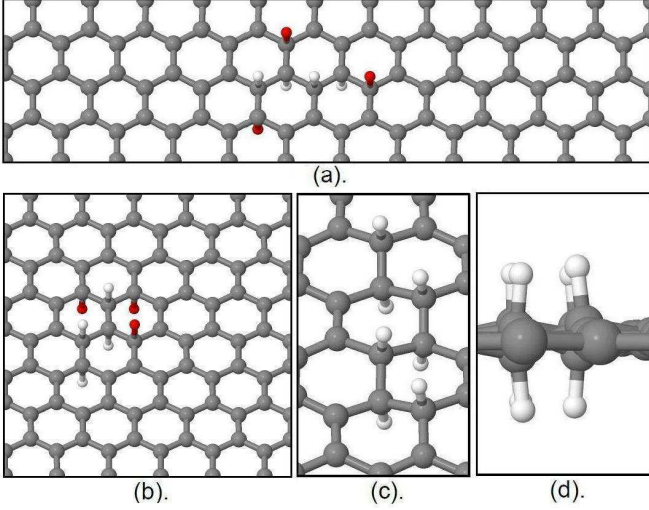


FIG. 1: (a) A schematic depiction of the supercell for the armchair strained graphene. (b) That for the zigzag strained graphene. The red atoms denote possible adsorbing sites whose adsorption energy will be evaluated. (c) and (d) show two perspectives on the final, seven adatom configuration with zigzag strain. Note the structural distortion in (c) and the inward leaning of the adatoms in (d).

because this conforms to the sp^3 hybridizing configuration of the host carbon atom and minimizes structural distortion. After finding the energetically preferred position for the second adatom, we can continue this search procedure to find those positions for the third and fourth adatoms and so on. We illustrate two examples of this process in Figs. 1 (a) and (b), where four hydrogen atoms shown in white are fixed adsorption adatoms and those in red are the possible sites we consider for the fifth adatom. Because of the symmetry, other nearest neighbor sites are symmetrically equivalent to the three shown in Figs. 1 (a) and (b).

We have investigated the adsorption energy for two types of strain, zigzag and armchair, respectively. The adsorption energies of patterns under these two strain conditions exhibit qualitatively different behaviors as shown in Fig. 2 (a), where we plot the energy difference between the chain configuration, which is defined by the regular pattern perpendicular to the strain, and the alternative configuration with the lowest energy.

In the zigzag strain case, we check the adsorption energy up to seven hydrogen adatoms. The energetic favorability of the chain configuration is always positive, meaning the chain configuration along the armchair direction is the energetically preferred adsorption pattern, depicted in Figs. 1 (c) and (d). For most cases, the adatom adsorbed along the armchair direction is preferred by around one hundred meV. This values of the energy gain could be tuned by choosing other chemical adsorption groups, which is important for the self assembly of these patterns. This general preference to grow a pattern perpendicular to the strain can be under-

stood in terms of the change in the orbital hybridization upon adsorption. After hydrogen atoms are adsorbed onto graphene, the hybridization of host carbon atoms changes from sp^2 to sp^3 , and the bond length between the nearest neighboring carbon atoms is extended. As a result, the perpendicular adsorption line is the best way to release the applied strain and lower the total energy.

Since the adsorption of hydrogen atoms on graphene involves a change in hybridization of host carbon atoms from sp^2 to sp^3 , it is of interest to study how the local chemical bonds change with the adsorption process. We plot the mean of the absolute deviation of host carbon atoms from the graphene plane for both the chain configuration and the second lowest energy configuration for zigzag strain in Fig. 2 (b). An interesting oscillating behavior is observed for the average height of host carbon atoms. We can explain this behavior in terms of a tight-binding model (see Refs. 22, 23 for details of this model) as the following.

When graphene is strained along the zigzag axis the C-C bonds along the zigzag bonds increase in length, while that along the armchair axis decreases in length after the full structural relaxation. Correspondingly, the tight-binding hopping parameters along the zigzag direction decrease, while that along the armchair direction increases. This leads to a dimerization of C-C bonds along the armchair direction. When the number of hydrogen atoms present on the graphene sheet is odd there is always a dimer with a single orphaned electron, and it is energetically preferable for the subsequent hydrogen to adsorb to the other carbon to form the dimer pair, substantially increasing the energy gain for adsorption patterns along the armchair direction. When an even number of hydrogen atoms are present, however, there is no such effect, and the placement of the next adatom is instead determined by reduction of structural distortion, which is a small energy gain. This explains the alternating pattern of the plot in Fig. 2 (b). This interpretation also sheds light on the notably small energetic favorability of the chain when there are four adsorbed hydrogens as shown in Fig. 2 (a). In this case because the chain is short, the net structural distortion is very sensitive to the placement of the fourth adatom, and this factor competes well with the dimerization effect. The two competing systems are shown in Fig. 3(a).

Meanwhile, we observe a strikingly different behavior in the case of armchair strain; a chain of adsorbed hydrogen adatoms begins to form along the zigzag direction. However, once the length of the chain reaches five atoms, the zigzag direction is no longer the energetically preferred configuration and the system depicted in Fig. 3(b) is preferred. Even more interesting is that the critical length of the chain is dependent upon the size of the supercell. In a supercell which is nine carbon atoms wide in the zigzag direction, the chain can only be held for up to three adatoms, while for a ten carbon wide supercell the chain can be held for up to six adatoms.

This supercell effect can be attributed to the inter-

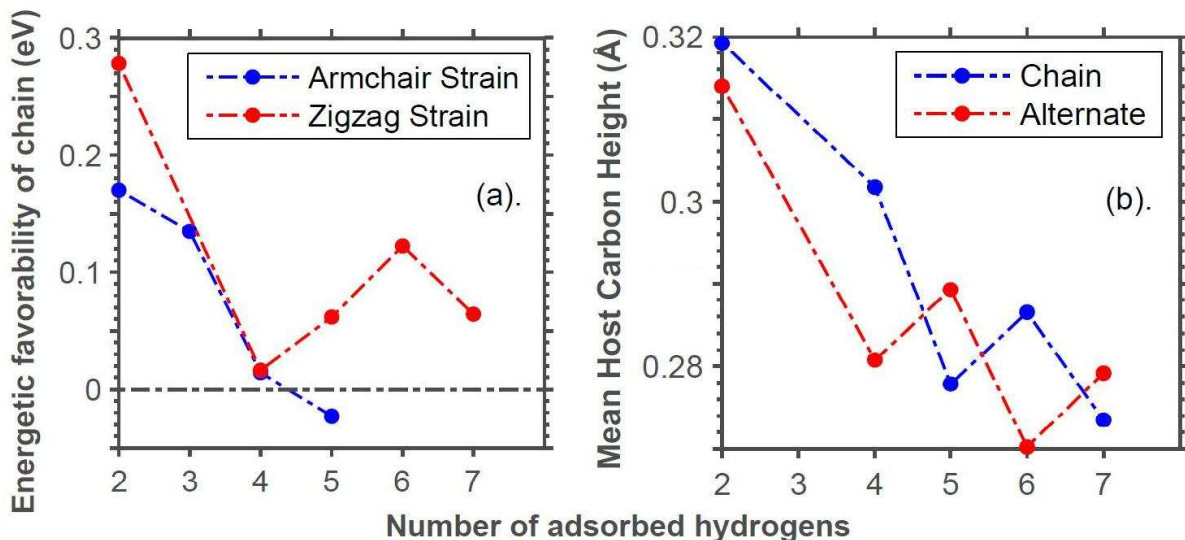


FIG. 2: (a) The plot of the relative energetic favorability of the chain configuration relative to lowest energy alternative configuration. Note that at five adatoms, the armchair strained system no longer prefers growth perpendicular to the strain. (b) The plot of the mean of the absolute vertical deviation of host carbon atoms from the graphene plane for zigzag strain. The chain configuration is always preferred; this plot illustrates the alternating influences of dimerization and minimization of structural distortion, as discussed above.

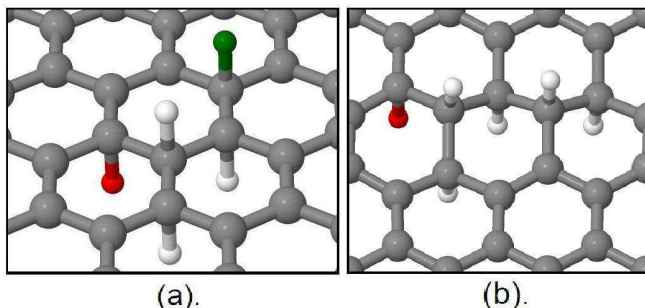


FIG. 3: (a) Two adatom placements whose energies differ by only 16 meV due to the competing influences of dimerization and minimization of structural distortion. The green adatom has lower energy due to the dimerization effect. (b) The preferred configuration for 5 adatoms on armchair strained graphene. The red adatom highlights the expected location of the fifth adatom without supercell resonance effects.

action between adsorption patterns with the electrons around the Dirac cones where the Fermi level is located. In graphene, those active electrons at the Fermi level have a characteristic wavelength determined by the position of the Dirac cones in the first Brillouin zone. As we vary the size of the supercell and the adsorption patterns, they can resonant with the Dirac electrons if the spacial frequency of the adsorption pattern has a component close

to the wavelength of the Dirac cones. This unusual formation energy change only occurs for the zigzag-directed pattern because the Dirac cones in our rectangular supercell lie along the zigzag axis [22]. Although this supercell effect is due to the limitations of periodic boundary conditions, it is of importance in the realistic dynamic self assembly of these patterns because their periodicity will be influenced by the same mechanism.

In summary, through first-principles calculations we have found that it is possible to direct adsorption patterns of hydrogen on graphene with the application of uniaxial zigzag strain. Although the energy gain is not extremely significant, it could be improved by choosing other chemical groups with a smaller binding energy. The results in the armchair case are not as positive due apparently to the limitations of periodic boundary conditions and associated enhanced perturbation from electrons around Dirac cones.

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